

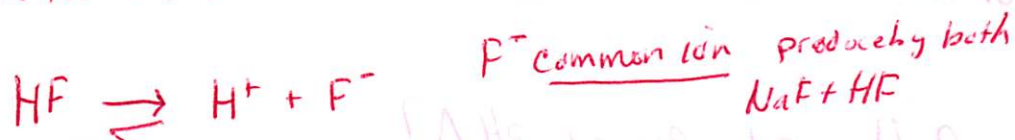
# Ch 15 Applications of Aqueous Eq.

## AB Equilibria

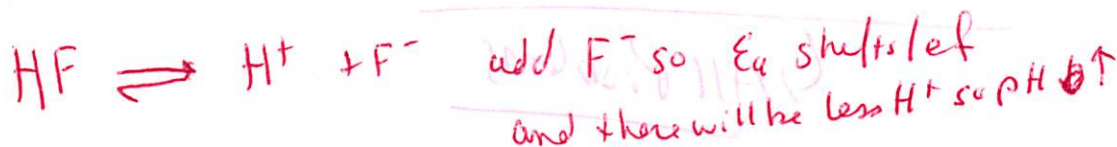
### 15.1 Solns w/ Common Ion

↳ weak acid + Conj Base

Soln of HF w/ NaF



What effect does common ion have on Eq?



Common ion effect - shift in Eq position b/c of addition ion already involved in Equilibrium

~~Do problem in ppt using common ion~~

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

$$0.01 = \frac{0.01}{0.25} \frac{[\text{H}^+]}{[\text{A}^-]} \quad \frac{0.01}{0.25} = 0.04 = \frac{[\text{H}^+]}{[\text{A}^-]}$$

# Buffer Solutions

↳ solution that resists pH change

Blood is buffered to absorb acids/base produced in biological processes w/out much pH change.

Buffers contain weak acid/base + its salt

How does a Buffer soln resist pH?

It's All Equilibrium!!

↳ All Problems

Do Common Ion problems / Buffer Problems

How Buffer works

$K_a = \frac{[H^+][A^-]}{[HA]}$        $[H^+] = K_a \frac{[HA]}{[A^-]}$       The OH<sup>-</sup> change HA to A<sup>-</sup>  
But if [HA] / [A<sup>-</sup>] are large  
Compared to [OH<sup>-</sup> added] Ratio changes  
very little so very small change

$$\frac{[HA]}{[A^-]} = \frac{0.50}{0.50} = 1.0 \xrightarrow{0.01} \frac{[HA]}{[A^-]} = \frac{0.49}{0.51} = 0.96$$

↑ Not Much Change

make the same argument using the Henderson-Hasselbalch Eqn

$$pH = pK_a + \log \left( \frac{[A^-]}{[HA]} \right)$$

useful to calculate pH when  $[A^-]/[HA]$  is known.

## Buffer Review

Buffer Capacity - the amount of  $H^+$  /  $OH^-$  a buffered soln can absorb w/o significant change in pH.

Large Cap  $\rightarrow$  large amount  $H^+$  /  $OH^-$  absorbed

Capacity depends on  $[HA]/[A^-]$

What determines Buffering Capacity?

Need Ratio of  $HA/A^-$  to be equal to 1. for most effective Buffer.

Making a Buffer

$\hookrightarrow$  want pH of 4.30

$\hookrightarrow$  so pick acid where  $pH = pK_a$  or as close as possible

if 4.30  $\rightarrow [H] = K_a = 5.0 \times 10^{-5} M$

Using mass

using neutralization

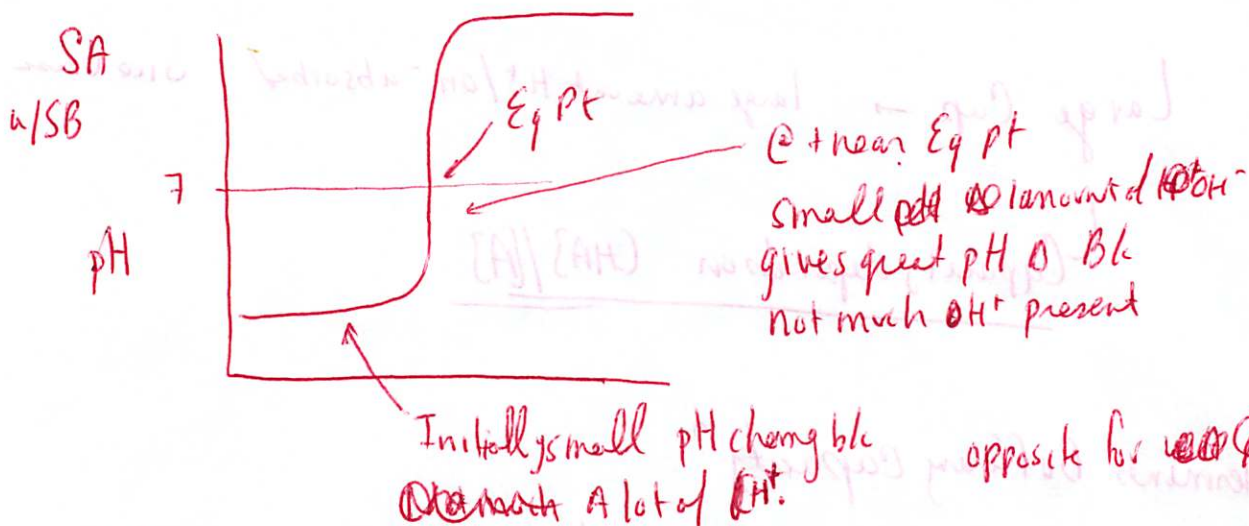


# Titration's - pH Curves

↳ measure [ ]

Here we will look @ pH changes in AB calc

## Basic pH Titration Curve



Calculations are all stoichiometric

Can determine pH @ any

V added B/c everything

dissociates

Handwritten notes:

$pH = 14 - pOH$

Handwritten notes:

Handwritten notes:

## Weak Titrations

↳ pH change must be calculated through Stoich then Equilibrium

Do Calc @ various amounts added

Differences - After Eq Pt Curves are same B/c  $\text{OH}^-$  governs the pH

WA → Bump b/c pH ↑ quickly

Then levels off B/c of Buffering Effect

↳ midpoint →  $[\text{A}^-] = [\text{HA}]$

Eq Pt SA → 7,

WA > 7 B/c of Basicity of conj Base

Stoichiometrically  
Determined

## Do Calculations

Notes → \* Amount of substance (A or B) determine Eq Pt

\* Eq Pt pH is affected by acid strength

\* Shape of curve as well.

\*  $\frac{1}{2}$  Eq Pt  $\text{pH} = \text{pK}_a$

## 15.5 AB Indicators

Two ways to see  $E_g$  Pt

1. pH meter + Tit Curve

2. Indicator



Color A

Color B

~~For phenolphthalein~~  $\rightarrow K_a = 1.0 \times 10^{-8}$

As more <sup>Base</sup> ~~Acid~~ is added more colored  $In^-$  exists

$$\text{visible color} \propto \frac{[In^-]}{[HIn]} = \frac{1}{10}$$

$$\text{So } pH = pK_a + \log \frac{1}{10}$$

↑  
color  
change

for Bromthymol Blue

$$pH = 1 \times 10^{-7} + \log 0.1$$

$$= 6$$

Select indicator whose color changes (End pt) is close to  
Equivalence Point

For Strong Acid  $E_g$   $pH$  is  $\sim 7$

4

$$7 = pK_a + \log \frac{1}{10}$$

$$\underline{pK_{a_{in}} = 8}$$

$$K_a = 1 \times 10^{-8}$$

$\uparrow$  so this indicator changes  $\sim pH = 7$

## Solubility Equilibria

$\hookrightarrow$  why important  $\rightarrow$  Tooth decay  $Ca_5(PO_4)_3OH \rightarrow$  more soluble in acid

$CaSO_4$  in Boilers Reduce thermal efficiency.

$BaSO_4 \rightarrow$  insoluble comp that is used for viewing internal tract.

Ions in soln are in equilibrium w/ their salt



when soln is saturated  $\rightarrow$  at eq Equilibrium

$$K_{sp} = [Ca^{2+}][F^{-}]^2$$

$\uparrow$  Solubility product constant.

Solids not present in

$K_{sp}$  b/c solid has

No. play in  $E_g$  (more

crushing means more

SA for ions to dissociate  
and Reform)



## Solubility vs Solubility Product Const

$K_{sp} \rightarrow$  is a  $K_{eq}$  and only has 1 value for a solid @ given temp

Solubility is an Equilibrium Position

↳ measured as  $\frac{\text{mol}}{\text{L}}$  @ given temp (higher T more soluble)

↳ common ion Solubility varies

Do simple  $K_{sp}$  Problems calc solubility from  $K_{sp}$

## Relative Solubilities

$K_{sp}$  does compare solubilities but must make sure to  
1. Compare same # of ions

AgI	$1.5 \times 10^{-16}$	$K_{sp} = X^2$ <u>in all cases</u>
CuI	$5.0 \times 10^{-12}$	
CuSO <sub>4</sub>	$6.1 \times 10^{-5}$	

2. Salts w/ different # of ions

can't compare directly to determine  $K_{sp}$   
must calc molar solubility.



# Common Ion Effect

What if common ion present?

pH + solubility



add to and remove  $\text{H}_2\text{O}$   
it dissolves.

How and acids work.

$\text{Ag}_3\text{PO}_4$  more soluble <sup>acid than</sup> in  $\text{H}_2\text{O}$  B/c

$\text{PO}_4^{3-}$  is a strong Base

Why caverns form.  $\text{CO}_2$  in Rain makes  $\text{H}_2\text{O}$  acidic  
and it dissolves  $\text{CO}_3^{2-}$  (limestone) as  $\text{CO}_2$  then escapes.  
limestone Refers to making stalactites / mites

## Precipitation

We will use  $Q$  (now called ion product)

$Q > K_{sp}$  ppt until  $K_{sp}$  reached

$Q < K_{sp}$  No ppt

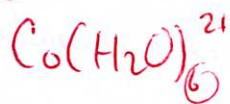
## Selective ppt

if 2 ions are present adding another to selectively ppt 1.

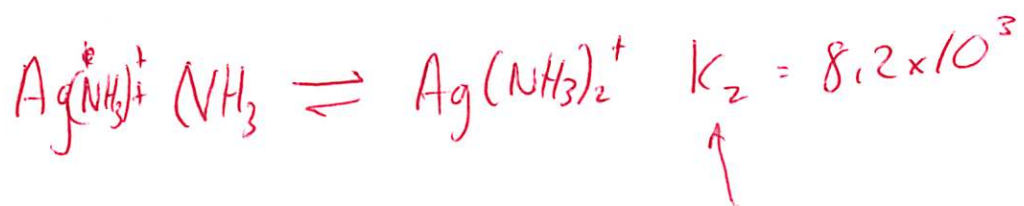
## Complex Ions

↳ Charged Metal ion surrounded by  
ligands - Lewis Base ( $e^-$  pair donor)  
( $H_2O$ ,  $Cl^-$ ,  $CN^-$ ,  $NH_3$ )

hof ligands  $\rightarrow$  coordination #



a Complexes form in multistep processes  
and have separate  $K$ :



all 4 species exist

Formation constants

But  $[\text{ligand}]$  v. high so problems are easier.

So only 2nd can be looked @

See problem

Prep a Buffer by adding 0.125 mol  $\text{NH}_4\text{Cl}$  to 500. mL of 0.500 M  $\text{NH}_3$ .

a What is the pH of Buffer

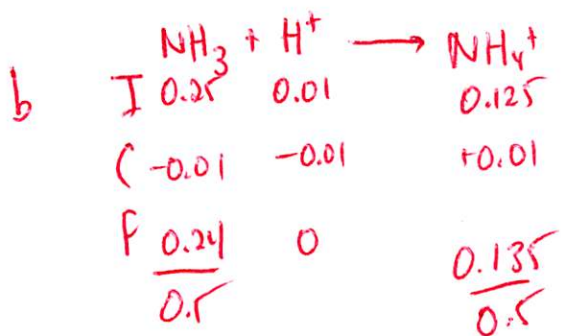
b If 0.0100 mol of  $\text{HCl}$  is bubbled into 500 mL of Buffer, what is the New pH?

$$[\text{NH}_4^+] = \frac{0.125 \text{ mol}}{0.500 \text{ L}} = 0.250 \text{ M } \text{NH}_4^+$$



$$\text{pH} \text{ or } \text{pOH} = \text{p}K_b + \log \frac{[\text{HA}^+]}{[\text{A}^-]}$$

$$4.74 + \log \frac{(0.250 \text{ M})}{(0.500 \text{ M})} = 4.74 - (14) = \boxed{9.556}$$



$$[\text{NH}_3] = 0.48 \text{ M}$$

$$[\text{NH}_4^+] = 0.27 \text{ M}$$

$$\text{pOH} = 4.74 + \log \frac{0.27 \text{ M}}{0.48 \text{ M}}$$

$$= 4.495$$

$$\text{pH} = 9.505$$

$$0.50 \text{ M} \times 0.500 \text{ L}$$